

CLASSIFICATION CONFIDENTIAL

CONFIDENTIAL

CENTRAL INTELLIGENCE AGENCY
INFORMATION FROM
FOREIGN DOCUMENTS OR RADIO BROADCASTS

REPORT

CD NO.

50X1-HUM

COUNTRY . USSR

DATE OF INFORMATION 1945

SUBJECT Scientific - Chemistry, Electrolytic metal
 refining

DATE DIST. 10 Sep. 1950

HOW PUBLISHED Monthly periodical

WHERE
PUBLISHED: Moscow; Leningrad

NO. OF PAGES 5

DATE
PUBLISHED Aug 1946

SUPPLEMENT TO
REPORT NO.

LANGUAGE Russian

THIS DOCUMENT CONTAINS INFORMATION AFFECTING THE NATIONAL DEFENSE OF THE UNITED STATES WITHIN THE MEANING OF ESPIONAGE ACT 50 U. S. C. 31 AND 32, AS AMENDED. ITS TRANSMISSION OR THE REVELATION OF ITS CONTENTS IN ANY MANNER TO AN UNAUTHORIZED PERSON IS PROHIBITED BY LAW. REPRODUCTION OF THIS FORM IS PROHIBITED.

THIS IS UNEVALUATED INFORMATION

SOURCE Zhurnal Prikladnoy Khimii, Vol XIX, No 8, 1946.

ELECTROLYTIC SEPARATION OF ZIRCONIUM

V. A. Plotnikov and E. B. Gitman

(submitted 17 Sep 1945)

[A Digest.]


Since work with an aqueous solution is easiest, we started our investigation of electrolytic separation of zirconium with a repetition of the electrolysis of aqueous zirconium sulfate according to Linford (1). Under the conditions described by Linford, we only obtained a black turbidity at the cathode together with a profuse evolution of hydrogen. Neither a brilliant deposit nor zirconium powder could be obtained by this method. This checks with the results reported by GIPKh (State Institute of Applied Chemistry) workers (2). Subsequently we experimented with melts, investigating the effects of temperature and current density at the cathode on the quality of the zirconium deposit separated electrolytically from the following mixtures: $\text{AlCl}_3\text{-KCl}-\text{NaF}-\text{ZrO}_2$; 2KF-ZrF_4 ; $\text{KCl}-\text{NaCl}-\text{K}_2\text{ZrF}_6$; $\text{KCl}-\text{NaCl}-\text{NaF}-\text{ZrO}_2$; $\text{ZrCl}_4-\text{NaCl}$.

Aluminium Chloride - Potassium Chloride - Sodium Fluoride - Zirconium Dioxide

Using 60 percent of aluminium chloride, 30 percent of potassium chloride, 6 percent of sodium fluoride, and 4 percent of zirconium dioxide (3), we obtained only a black powder at the highest zirconium content. Using other proportions, a brilliant alloy of aluminium with zirconium was deposited at current densities of 5-24 amperes per square decimeter. At current densities higher than that, the zirconium content diminishes in the brilliant deposit, while at current densities lower than 5 amperes per square decimeter, a black powder having a varying zirconium content is obtained. Ukrainian workers who first suggested the composition of the melt originally tested by us (3) reported obtaining with it brilliant deposits between 5-24 amperes and reduction of Zr content in the contiguous deposit at higher current densities, while the deposition of powdered material increased.

CONFIDENTIAL

CLASSIFICATION CONFIDENTIAL

CLASSIFICATION			CONFIDENTIAL		
STATE	<input checked="" type="checkbox"/> NAVY	<input checked="" type="checkbox"/> NSRB	DISTRIBUTION		
ARMY	<input checked="" type="checkbox"/> AIR	<input checked="" type="checkbox"/> FBI			

CONFIDENTIAL

CONFIDENTIAL

50X1-HUM

We used a copper cathode and a rod-shaped graphite anode which was protected from burning by a porcelain tube leaving free only the lower graphite tip (10-15 millimeters). The electrolysis was carried out in a porcelain beaker of 100-150 milliliters capacity. The zirconium powder dropping from the cathode was collected in a small porcelain beaker placed under the cathode. In almost all experiments the powder was completely recovered from the melt. The temperature was measured by a thermocouple dipping into the melt. The black crystalline powders were washed with warm water which had been acidified with hydrochloric acid. The amorphous precipitates, which were difficult to filter, were washed with an ammonium chloride solution.

The current density at the cathode was varied between 1 and 20 amperes per square decimeter at temperatures of 360-550°C. The potential applied at the contacts of the electrolytic bath was between 3 and 5 volts. For analysis the powder was fused with bisulfate and the zirconium precipitated as its pyrosulfate (this method for determining the zirconium was also used in the case of powders obtained from other melts). In view of the fact that a thin insoluble layer of electrolyte remained on the surface of the powder, the values determined by this method were slightly too low.

As can be seen from Table 1, the highest content of zirconium in the powder amounted to 71 percent at a current density of 7 amperes per square decimeter. Temperature changes in the range indicated above had no influence on the quality of the deposit. The powders caught fire in the air at a temperature of about 400 degrees centigrade, while powders obtained by thermic reduction had already caught fire at 210 degrees centigrade. The presence of a thin layer of electrolyte on the surface in the first case may be the explanation for that difference in behavior.

Potassium Fluorozirconate (4)

The double salt was prepared by dissolving zirconium dioxide in hydrofluoric acid and then adding a stoichiometric quantity of potassium fluoride. The electrolysis was carried out in a carbon beaker. The cathode was a molybdenum or iron plate while a carbon rod served as the anode. The carbon beaker was placed into an electric crucible furnace. At 500 degrees centigrade after 2-2½ hours of electrolyzing, potassium fluoride precipitated at the bottom of the beaker. At about that time the separation of black zirconium powder stopped. One may assume that at this temperature the hexafluorozirconate of potassium decomposes under volatilization of zirconium fluoride. The electrolysis was carried out at current densities of 0.5-15 amperes per square decimeter. At 0.5 ampere per square decimeter in one instance an adhering layer of zirconium metal appeared in spots on the molybdenum cathode. This later was covered by a fine gray powder. At all other current densities a gray powder having a zirconium content of 63-70 percent was separated.

Potassium Chloride - Sodium Chloride - Potassium Hexafluorozirconate

In order to eliminate the rather high volatility of potassium hexafluorozirconate, we used a less volatile mixture which was mentioned in a USA patent (5) and investigated by GIPKh workers (2), namely, a low-melting, eutectic mixture of sodium chloride and potassium chloride to which 5-35 percent of potassium hexafluorozirconate had been added. Since neither the US patent nor the GIPKh report mention any details, we investigated this system at various current densities, temperatures, and potassium hexafluorozirconate concentrations. On melting, the mixture is transparent, mobile, and not very volatile. It is not hydrolyzed by the moisture of the air. On melting of the sodium chloride-potassium chloride mixture (after these salts had been purified and remelted), a graphite anode protected by a corundum pipe is dipped into the mixture. Thereupon potassium hexafluorozirconate is added and a molybdenum or iron cathode is lowered after the current has been switched on.

- 2 -

CONFIDENTIAL

CONFIDENTIAL

CONFIDENTIAL

CONFIDENTIAL

50X1-HUM

In order to maintain a constant composition, fresh potassium hexafluorozirconate is added to the mixture every 30-35 minutes. The electrolysis is carried out in a porcelain beaker or an iron crucible. It is necessary to substitute a new cathode for the old one from time to time, because deposition on the old one ceases after a while. Experiments were carried out at temperatures starting with 660 degrees centigrade (fusion temperature of the salt mixture) and going up to 800 degrees centigrade. The best deposits having the highest zirconium content result at 660-700 degrees centigrade. Above 700 degrees centigrade the zirconium powder oxidizes. Increasing the potassium fluorozirconate concentration from 5 to 20 percent has no perceptible effect on the quality of the deposit. At 700 degrees centigrade with a K_2ZrF_6 concentration of 20-35 percent and with a current density of 0.5 ampere per square decimeter, we were able to obtain a zirconium powder consisting of large granules. At that current density, the powder has the highest zirconium content. Thin, brittle zirconium plates are occasionally deposited on the cathode at the same current density. It could be established by microscopic examination that these plates consist of individual zirconium crystals which have grown together. With this procedure, the current yield is somewhat higher than 50 percent. The powder catches fire at 450-500 degrees centigrade. The results obtained in this instance are given in Table 2. Under conditions described here, the GIPKh workers (2) reported obtaining gray crystals of zirconium in an iron crucible with a current yield of 46.5 percent. They also mentioned the separation of a dense contiguous Zr deposit from molten K_2ZrF_6 on a cathode heated to 1,400 degrees centigrade.

Potassium Chloride - Sodium Chloride - Sodium Fluoride - Zirconium Dioxide

Since this mixture of salts does not involve the use of hexafluorozirconate, the process is simplified in this respect. Sodium fluoride has the function of dissolving the zirconium dioxide, but the solubility in the neighborhood of 700 degrees centigrade is rather low. The properties of the cathodic deposit in the range of current densities of 1 to 15 amperes per square decimeter have been investigated. At 15 amperes of density an amorphous mass which spreads throughout the volume of the melt is separated; at one ampere per square decimeter no zirconium at all is separated. At all other densities a grayish-black powder containing up to 50 percent Zr is obtained.

Zirconium Tetrachloride - Sodium Chloride

We prepared zirconium tetrachloride from black zirconium powder supplied by the Moscow Institute of Rare Metals. The zirconium powder was freed from iron by multiple washing with dilute hydrochloric acid. On drying it was briquetted with ten times the quantity of wood charcoal. The briquettes were charged into a porcelain tube which was placed into a nichrome tubular furnace. On removal of moisture, a stream of dry chlorine (dried very thoroughly with sulfuric acid and phosphorus pentoxide) was blown through the tube at 600-650 degrees centigrade. A ball receptacle was attached to the end of the tube. The highly volatile zirconium tetrachloride was deposited at the bottom of the balls. Chemically pure sodium chloride (reagent grade) was used. The salt was dissolved in water and crystallized while a stream of hydrogen chloride was passed through the solution. The crystals were washed with ice water and dried at a temperature of 450-500 degrees centigrade. To prevent hydrolysis, zirconium tetrachloride was fused with sodium chloride immediately upon preparation. The melt was stored in sealed test tubes.

We submitted to electrolysis the least volatile mixture having the composition $ZrCl_4 \cdot 4NaCl$, at a temperature of 550 degrees centigrade. A porcelain beaker equipped with a tightly fitting cover, to prevent escape of zirconium tetrachloride through volatilization, was used for electrolyzing the mixture. At current densities of 0.5-10 ampere per square decimeters, a black powder containing 80-85 percent of zirconium was obtained.

- 3 -

CONFIDENTIAL,

CONFIDENTIAL

CONFIDENTIAL

CONFIDENTIAL

50X1-HUM

We determined the decomposition potential at various temperatures for the mixture consisting of 50 percent zirconium tetrachloride and 50 percent sodium chloride. The values of the decomposition potential were determined from V-I curves. The measurements were carried out in a quartz test tube which was tightly closed by means of an asbestos stopper. A narrow molybdenum strip formed the cathode, while a graphite rod which had been previously chlorinated anodically for 2 hours served as the anode. The cathode was shielded by a narrow glass test tube having a hole near the bottom. This hole was plugged with asbestos serving as a diaphragm. The whole arrangement was placed into an electric furnace. The temperature was measured by means of a platinum-platinum-rhodium thermocouple and held constant within a span of plus 2 degrees centigrade. The current was measured with a milliamperemeter, while the potential was determined by means of a precision voltmeter having a scale graduated in 0.02 volt divisions. The V-I curves were taken both with rising and falling temperatures. Coincidence of points obtained in different experiments was observed.

The decomposition potential reached 2.0 volts at 550 degrees centigrade and amounted to 1.8 volts at 600 degrees centigrade. The decomposition potential falls rectilinearly with rising temperatures, the temperature coefficient being 3×10^{-3} volts per degree centigrade. It was not possible to determine the decomposition potentials at temperatures above 620 degrees centigrade owing to excessive volatility of the zirconium tetrachloride.

For purposes of comparison, it may be mentioned that chemical reduction of zirconium dioxide results in highly dispersed black powders which are contaminated by oxides, carbides, nitrides, and other admixtures (6). Purer powders are obtained by reducing zirconium tetrachloride or potassium hexafluorozirconate with alkali metals.

Bibliography

1. W. F. Bradt and H. B. Linford, Transactions Am. Electrochem. Society, Vol LXX, p 431, 1937
2. GIPKh Report No 96, 1937
3. Zap. Inst, Khimii AN URSR (Transactions of the Chemical Institute of the Academy of Sciences, Ukrainian SSR), I, 1939
4. L. Troost, Comptes rendus. Vol LXI, p 109, 1865; Vol CXVI, pp 1227, 1428 (1893)
5. Driggs, Bloomfield, and Lilliendahl, US Patent No 1 835 025, 8, XII, 1931
6. E. I. Krech, Zhurnal Prikladnoy Khimii (Journal of Applied Chemistry), No 10-11, p 1931, 1937

[Tables follow]

- 4 -

CONFIDENTIAL

CONFIDENTIAL

CONFIDENTIAL

CONFIDENTIAL

50X1-HUM

Table 1. Zirconium - Aluminium Alloy Separated from the Mixture
Aluminium Chloride - Potassium Chloride - Sodium Fluoride - Zirconium Dioxide

<u>Experi- ment</u>	<u>Current Density at Cathode (amp/sq dm)</u>	<u>Powder composition</u>		<u>Properties of Deposit</u>
		<u>Zr (%)</u>	<u>Al (%)</u>	
1	20	-	-	Amorphous precipitate
2	10	30	20	Black crystalline powder
3	7	71	13	" " "
4	5	50	6.2	" " "
5	2	50.3	6.3	" " "

Table 2. Zirconium Separated from the Mixture
Potassium Chloride - Sodium Chloride - Potassium Hexafluorozirconate

<u>Experi- ment</u>	<u>Current Density at Cathode (amp/sq dm)</u>	<u>Powder analysis</u>		<u>Properties of Deposit</u>
		<u>Zr (%)</u>	<u>Insoluble Residue (%)</u>	
1	20	65.6	5.2	Amorphous powder which is dif- ficult to filter
2	10	71.7	18.9	Grayish-black amorphous powder
3	3	77.2	18.1	Black powder
4	1	74.3	15.6	" "
5	0.5	90.0	10.0	Gray powder - large crystals under microscope

- E N D -

- 5 -

CONFIDENTIAL

CONFIDENTIAL